New Ligands for Hafnium Oxide Nanoparticle EUV Resists

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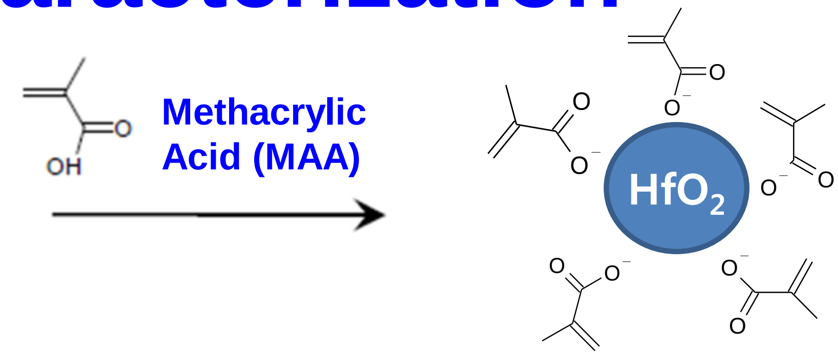
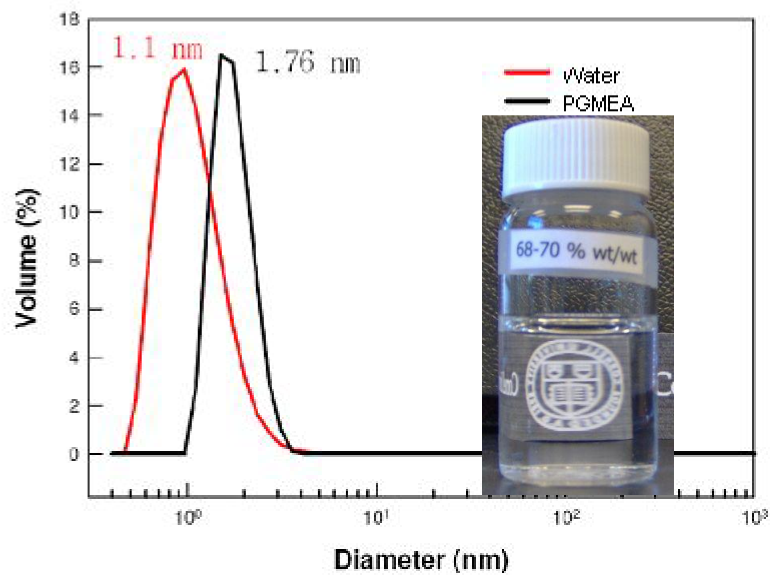
I. Introduction
II. Ligand Binding Study
III. Strong Binding Free Radical Monomers
V. Summary and Future Directions

Nanoparticle Synthesis and Characterization

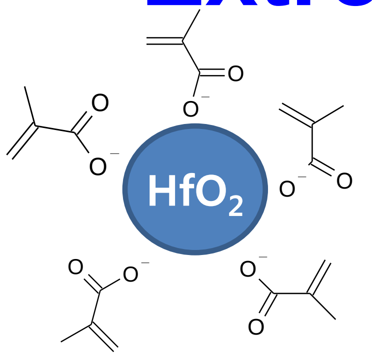
$Hf(iPrO)_4 + H_2O$



- Small particle size
- Stable suspensions

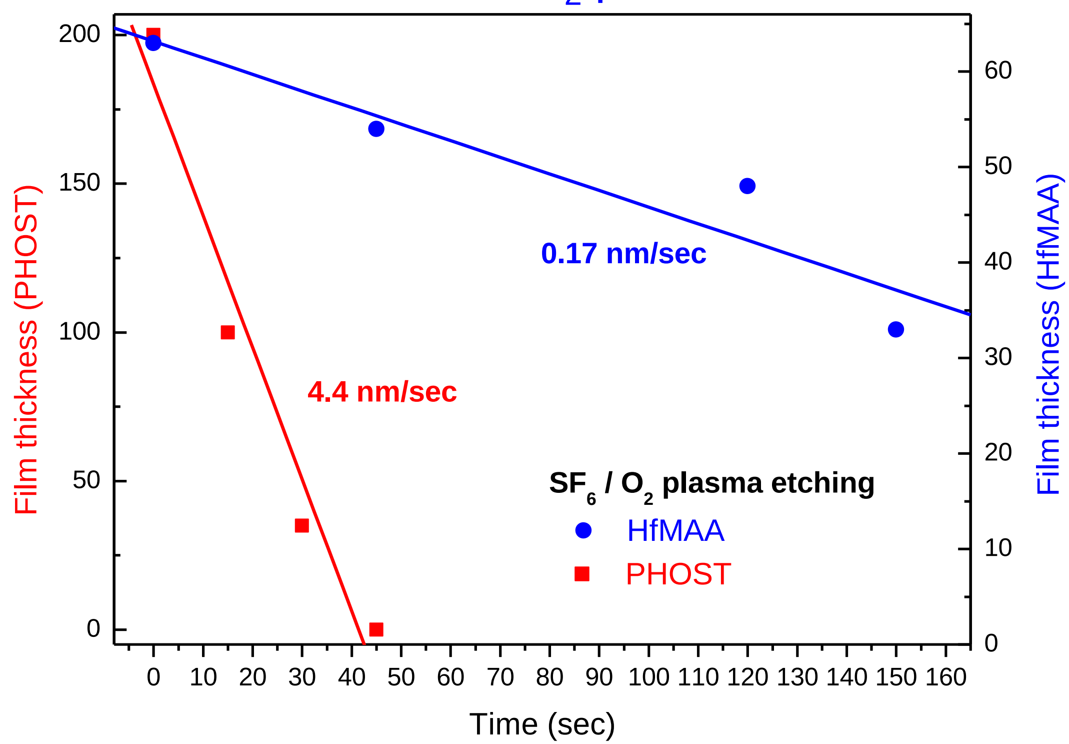


Extremely High Etch Materials



Etch Rate: ~25x PHOST in SF_6/O_2 Etch
Dual Tone Capabilities
Thermally stable below 120 ^oC

Patterned HfMAA films treated with O_2 plasma to increase etch resistance



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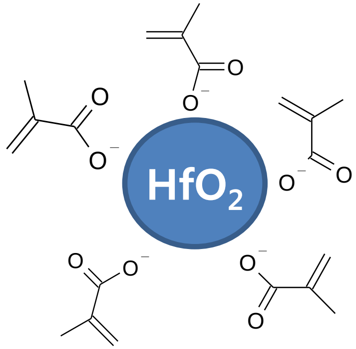
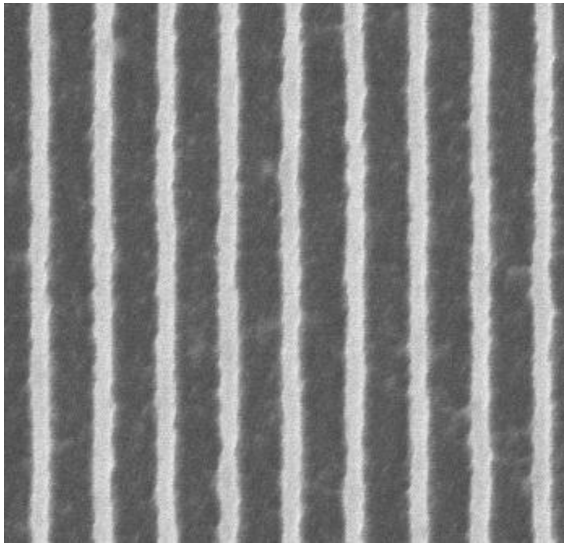
EUV Imaging

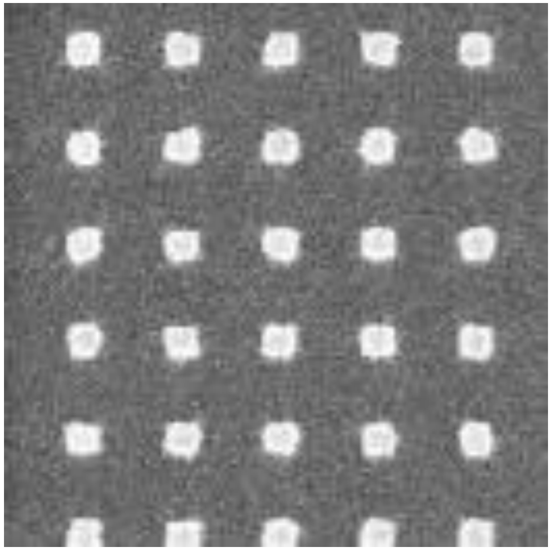


Etch Rate: ~25x PHOST in SF_6/O_2 Etch
Dual-tone capabilities
Thermally stable below 120 °C

Please see Cornell poster: "High etch resistance EUV resist based on inorganic nanoparticles"

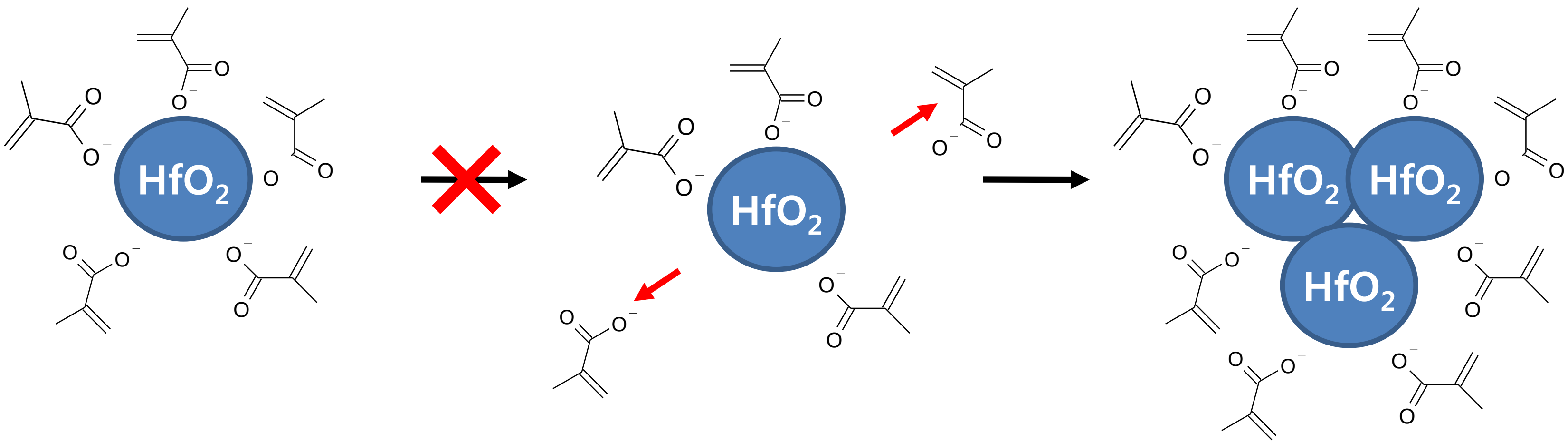


31 nm lines, 1:2 line:space
Dose: 7 mJ/cm^2



34 nm posts
Dose: 7 mJ/cm^2

II. Ligand Binding Strength



Without a strong ligand-nanoparticle bond, agglomeration can occur.

Plans to increase bond strength include:

1. Ligand binding study (Thermodynamics)

2. Strong-binding free-radical monomers

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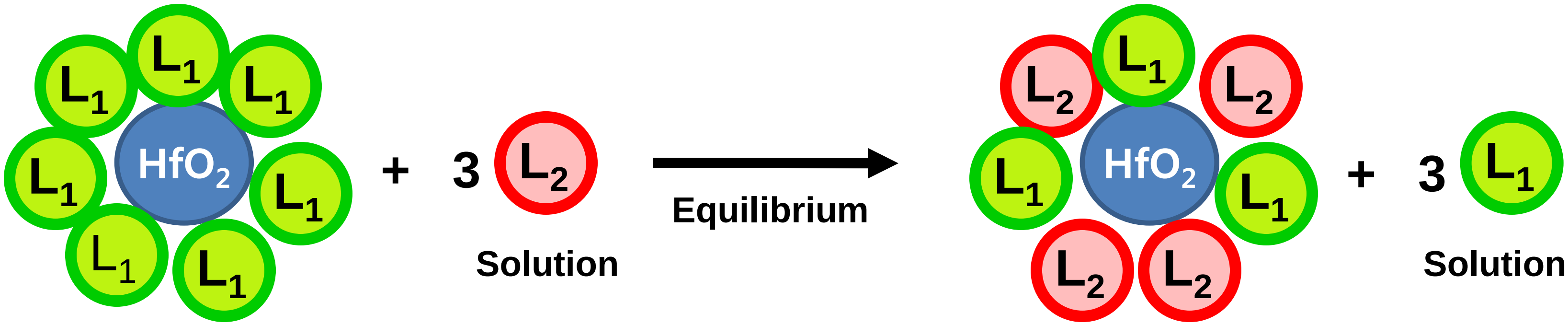
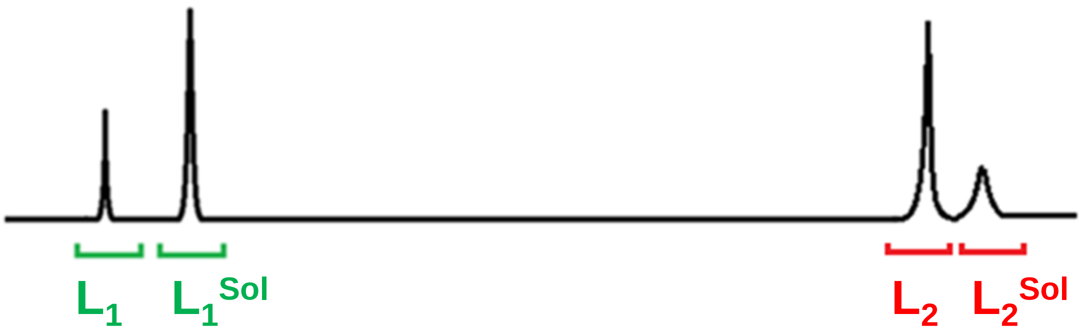
Pair-wise Comparison of Ligands





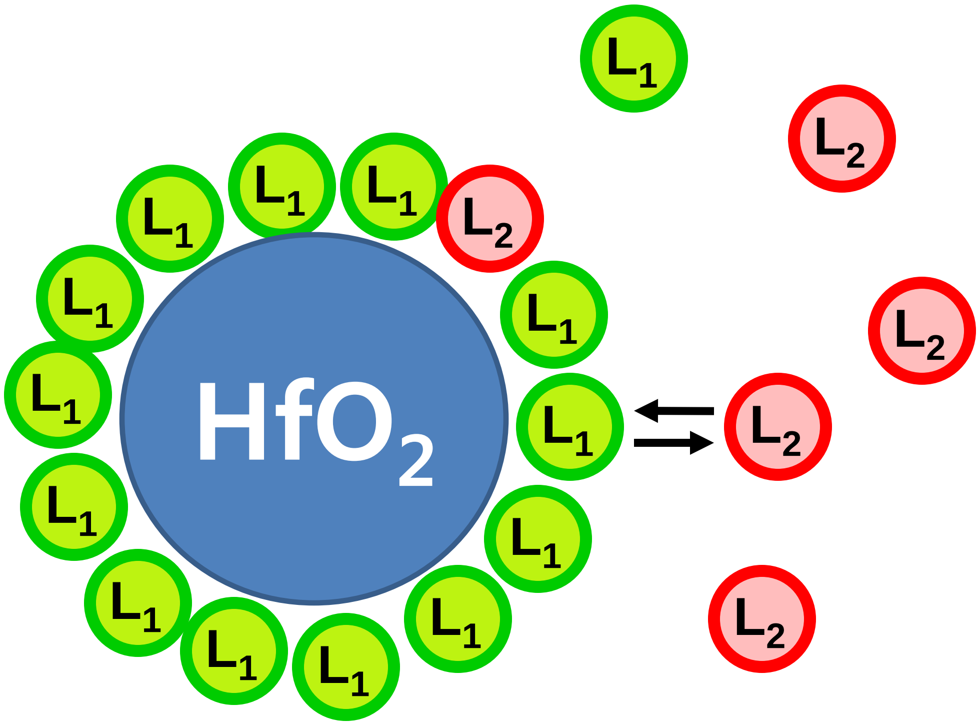
$$Keq = \frac{[L_2][L_1^{Sol}]}{[L_2^{Sol}][L_1]}$$

$$\Delta\Delta G^o = -RT \ln Keq$$

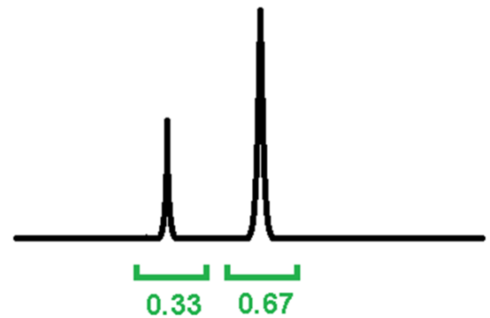
Relative Binding Energy Determination:

- Combine nanoparticles in a solution of mixed ligands.
- Measure equilibrium concentration of both ligands free in solution and bound to nanoparticles.

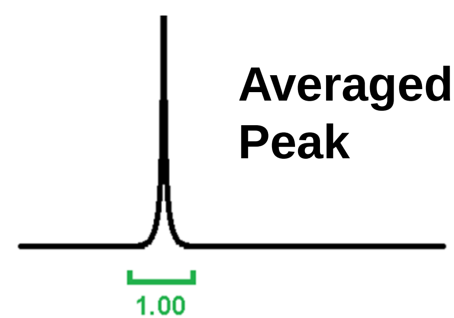
NMR Averaged Ligand Exchange



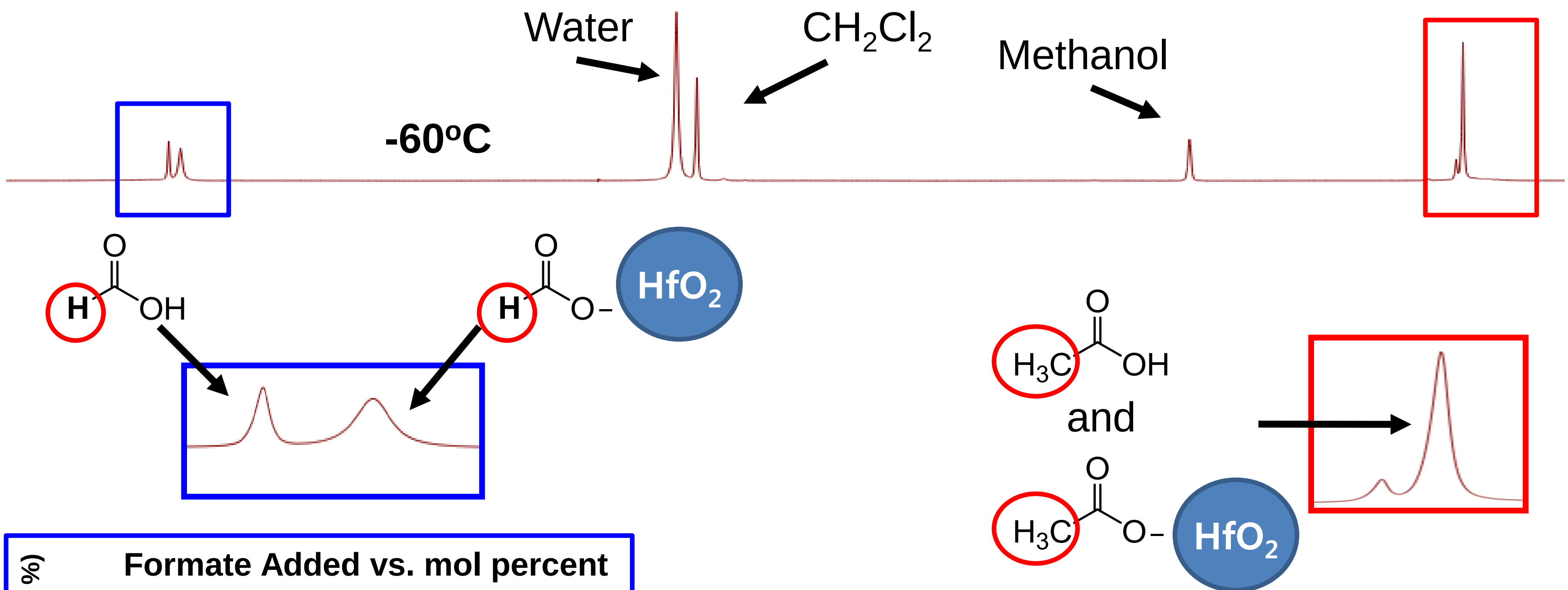
Expected Result:

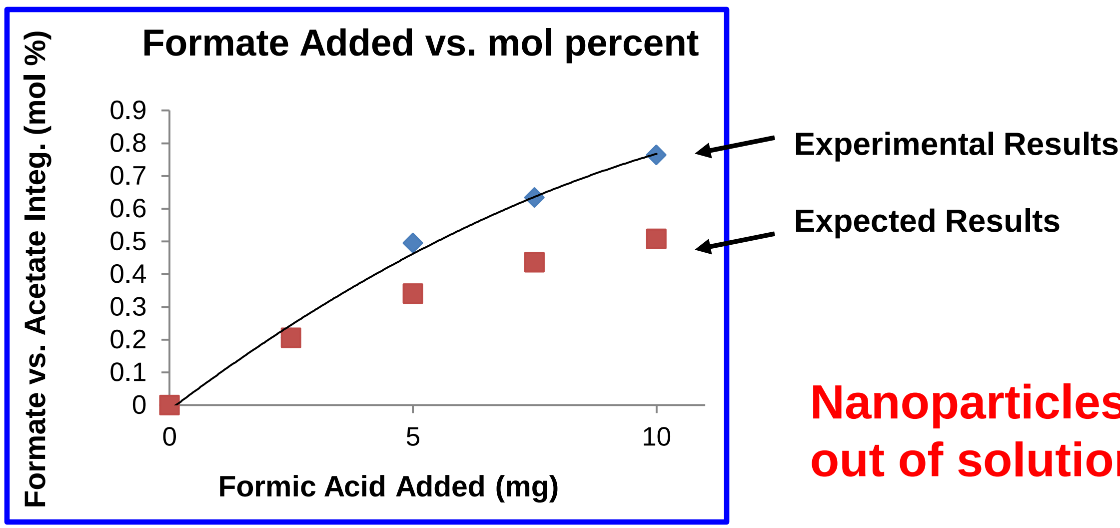


Exchange was too fast in the *timescale* of the NMR, resulting in peak averaging.



Formic Acid Nanoparticle NMR Exchange





Nanoparticles precipitated out of solution.

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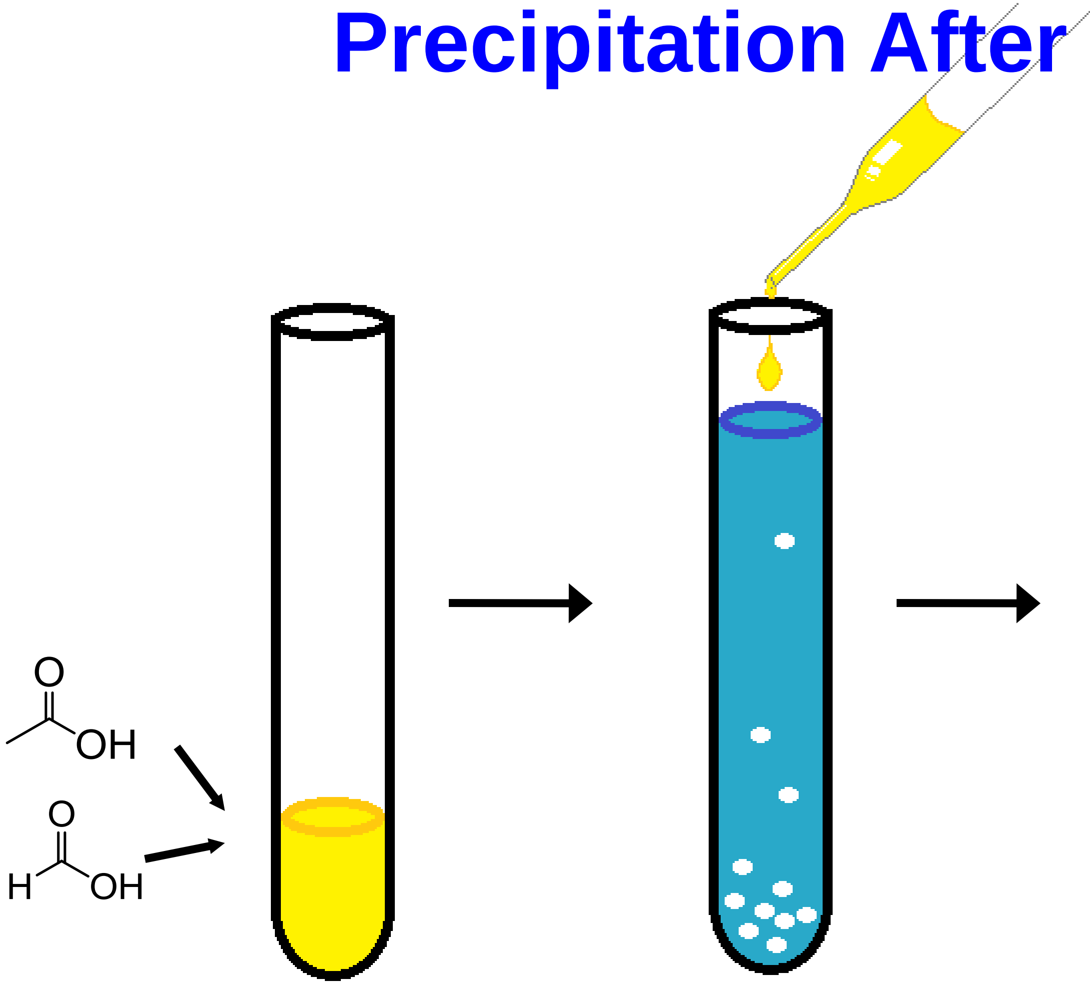
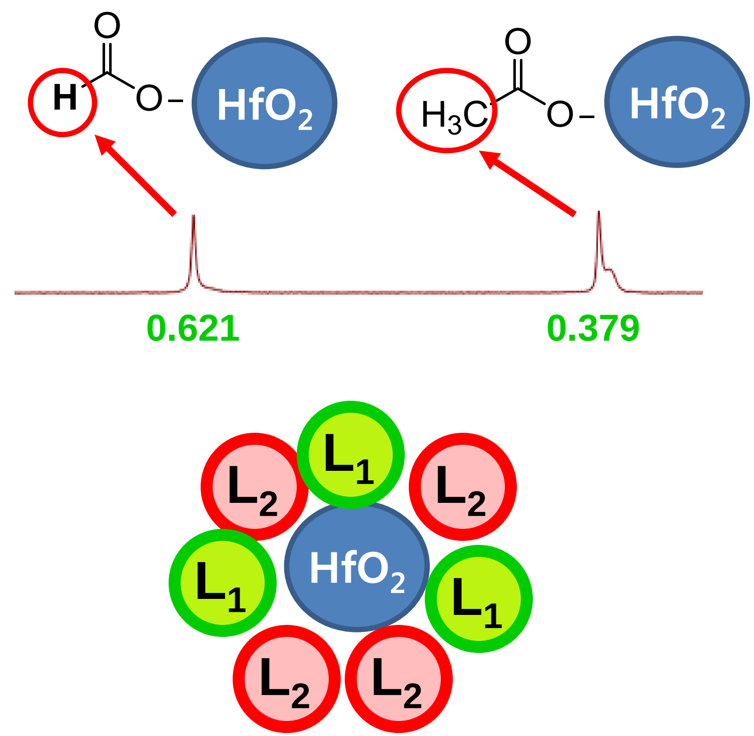
Precipitation After Exchange

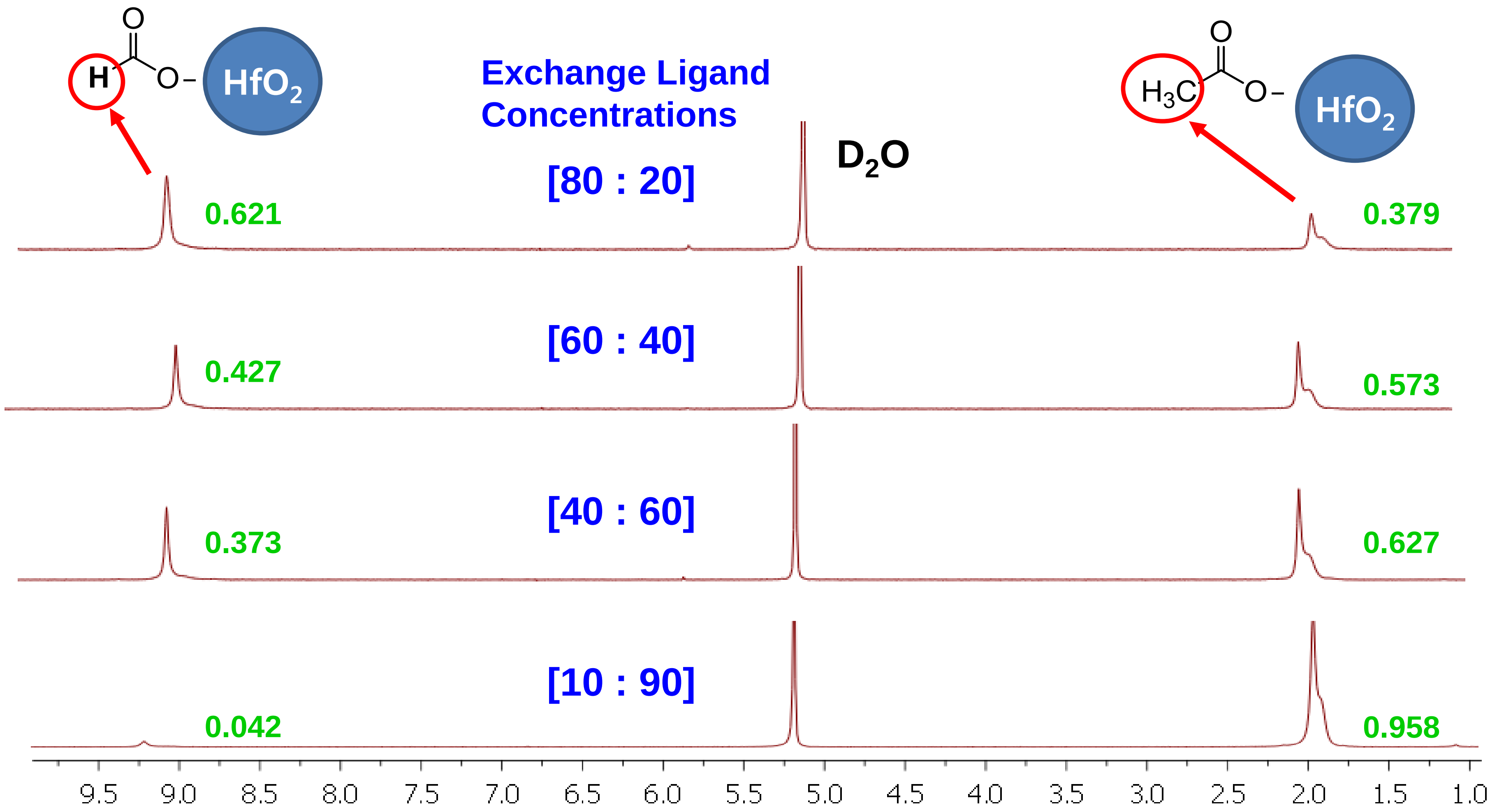


Perform exchange in neat ligand

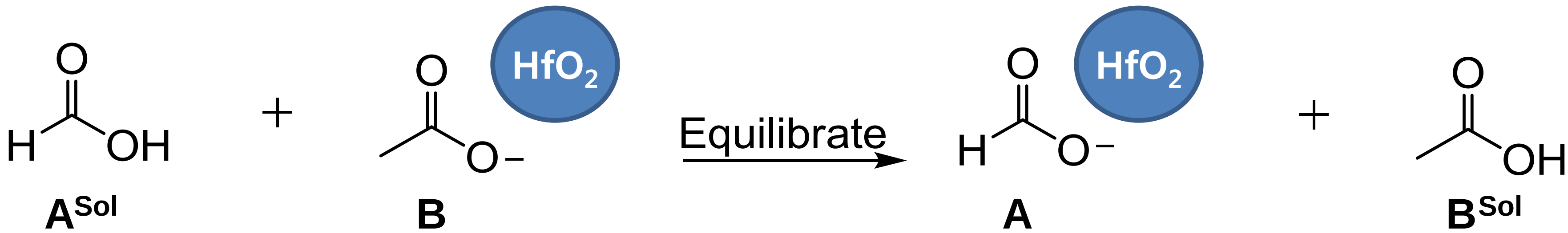
Precipitate/ Wash three times

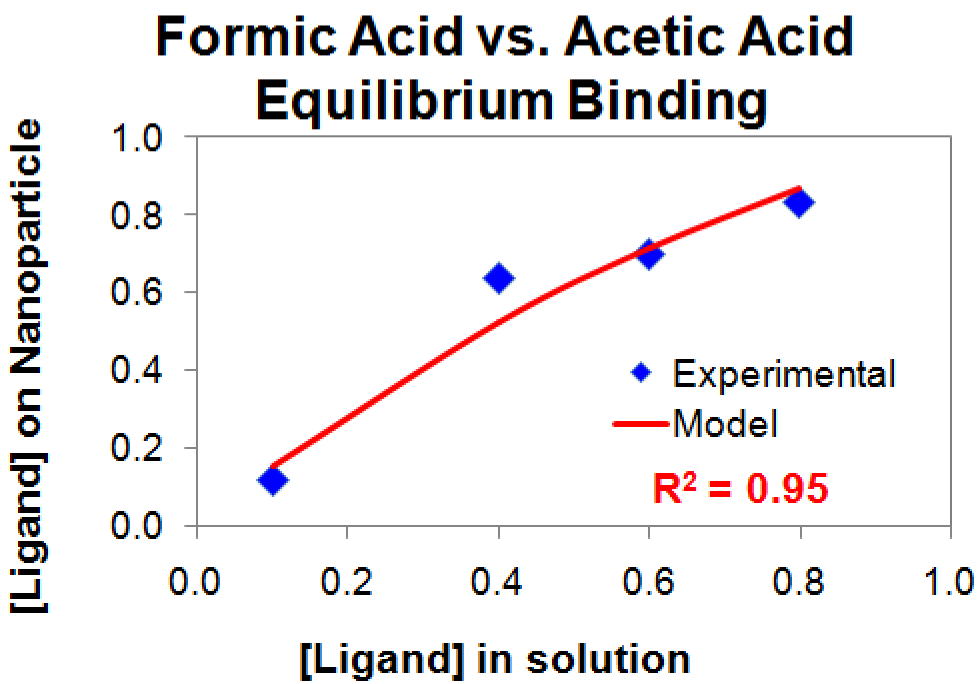


Nanoparticle Exchange / Precipitation



III. Relative Binding Energy of Formic Acid





$$Keq = \frac{[A][B^{Sol}]}{[A^{Sol}][B]}$$

$$\Delta\Delta G^o = -RT \ln Keq$$

Keq = 1.7

$\Delta\Delta G^o$ = -0.30 Kcal/mol

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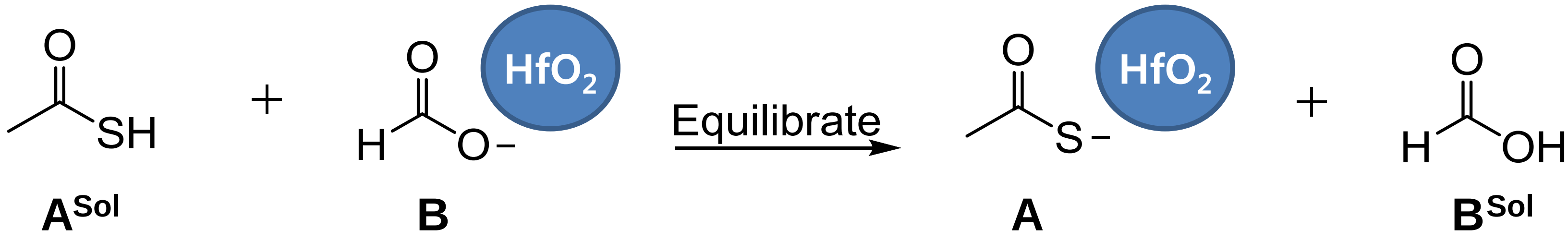
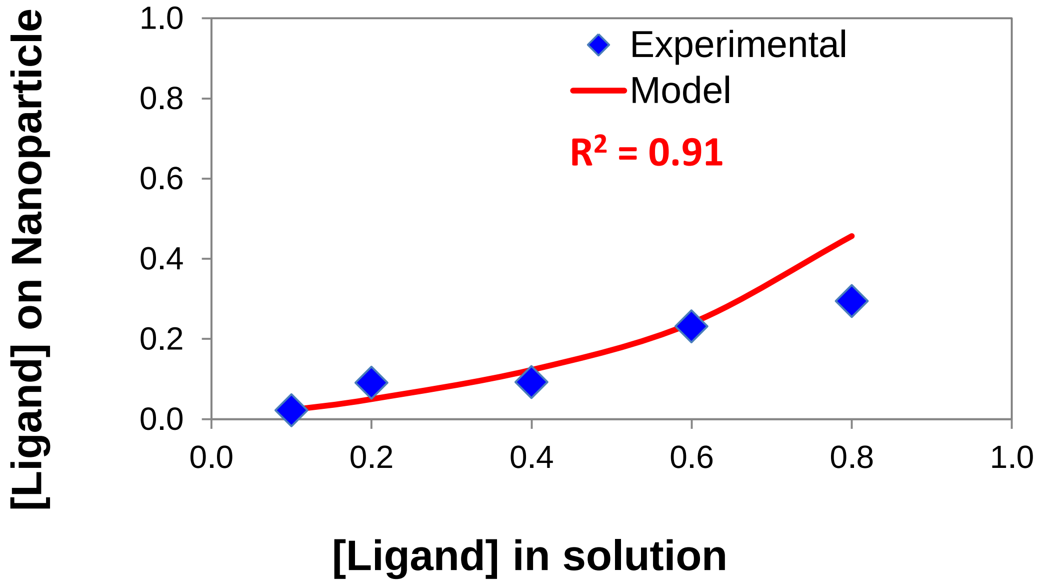
Relative Binding Energy of Thioacetic Acid



Thioacetic Acid vs. Formic Acid Equilibrium Binding



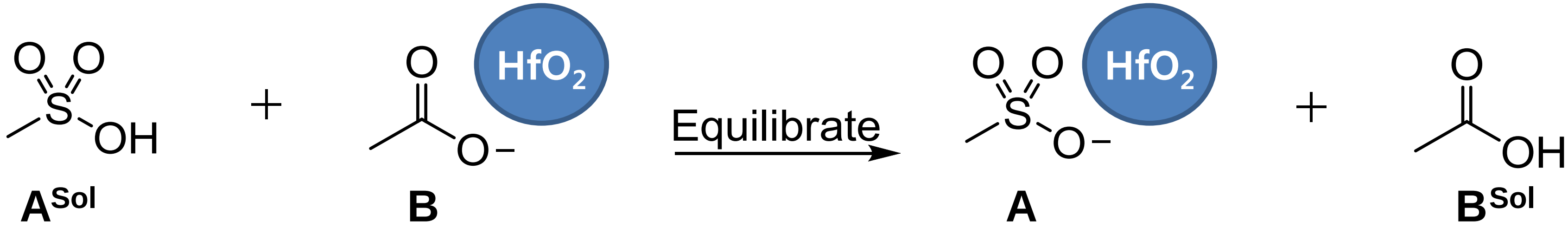
$$Keq = \frac{[A][B^{Sol}]}{[A^{Sol}][B]}$$

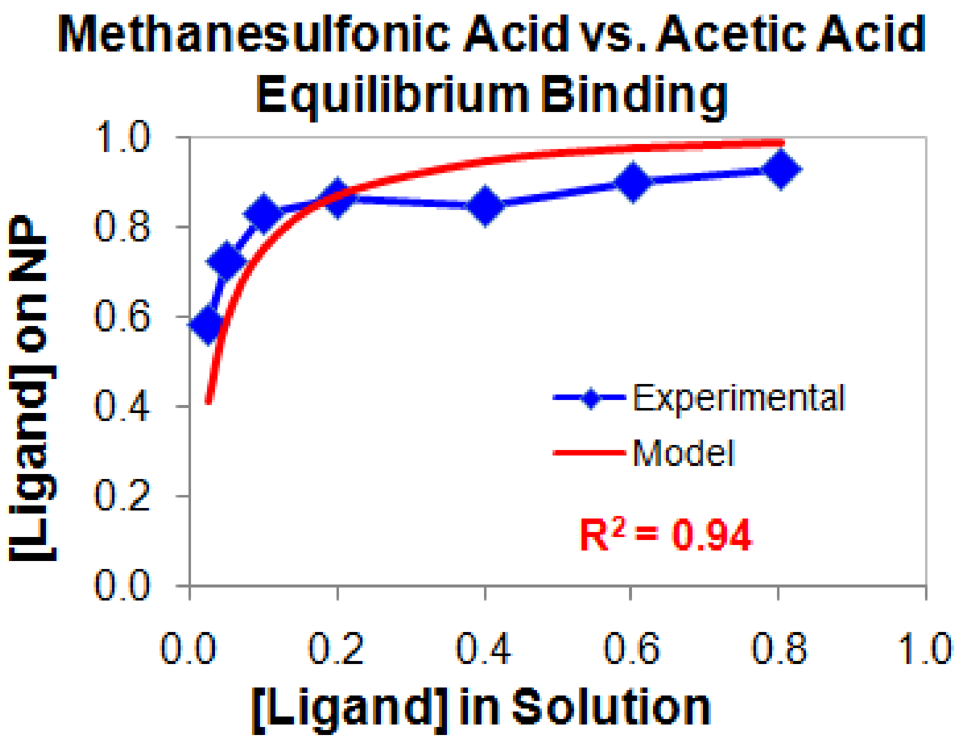
$$\Delta\Delta G^o = -RT \ln Keq$$

Keq = 0.2

$\Delta\Delta G^o$ = +0.93 Kcal/mol

Rel. Binding Energy of Methanesulfonic Acid





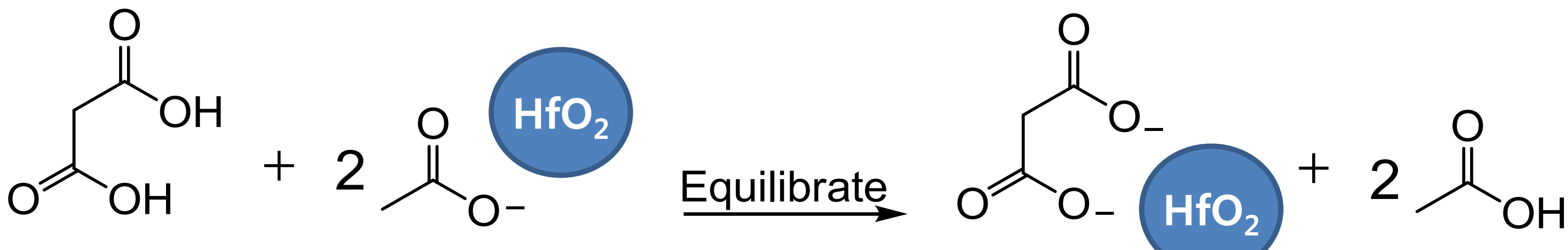
$$Keq = \frac{[A][B^{Sol}]}{[A^{Sol}][B]}$$

$$\Delta\Delta G^o = -RT \ln Keq$$

Keq = 27.8

$\Delta\Delta G^o$ = -1.96 Kcal/mol

Relative Binding Energy of Malonic Acid



A^{Sol} B A B^{Sol}

Raw Data:

[Ligand] sol'n	[Ligand] on NP
0.01	0.021
0.02	...
0.03	...
0.04	...
0.05	...

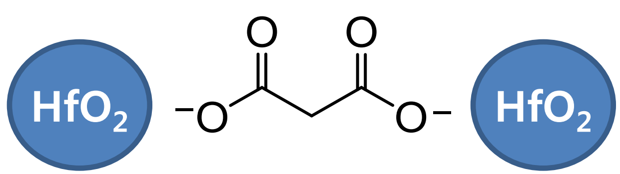
Insoluble

$$\boxed{Keq = \frac{[A][B^{Sol}]}{[A^{Sol}][B]}}$$

$$\boxed{\Delta\Delta G^{o} = -RT\ \ln Keq}$$

Keq = 2.0

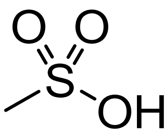
$\Delta\Delta G^{o}$ = -0.41 Kcal/mol



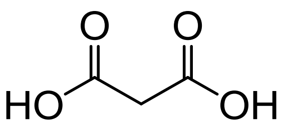
Forms a cross-linked insoluble matrix.

Relative Binding Energy Summary

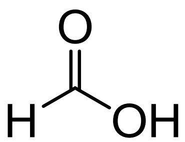
Relative Binding Energies (Kcal/mol) (Relative to Acetic Acid):



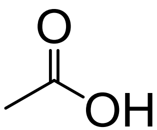
-1.96



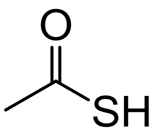
-0.41



-0.30



0.00

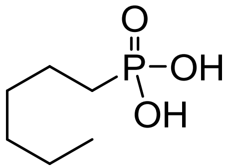
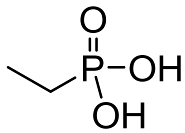
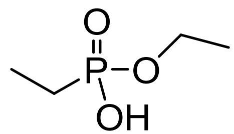


+0.63¥

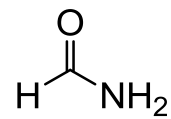
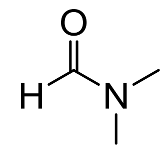
Stronger Binding Ligands

¥ - Related to acetic acid through the formate-acetate binding energy

Other Ligands Tested

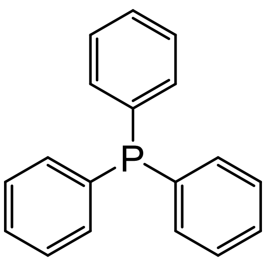




Form insoluble precipitate:
(insoluble in Hexane, Methylene Chloride, Toluene, Ether, THF, Ethyl Acetate, Acetone, Methanol, DMSO, Water)

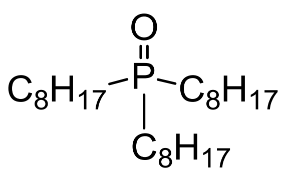



We were unable to separate nanoparticles and free ligands.

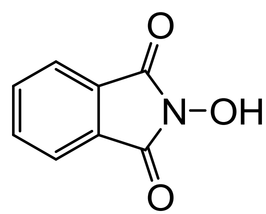
Relative Binding Energies Relative to Acetic Acid (Kcal/mol)



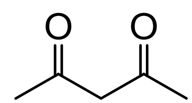
> +3.7



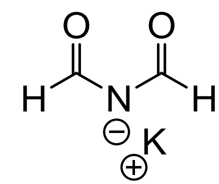
> +4.3



> +2.9



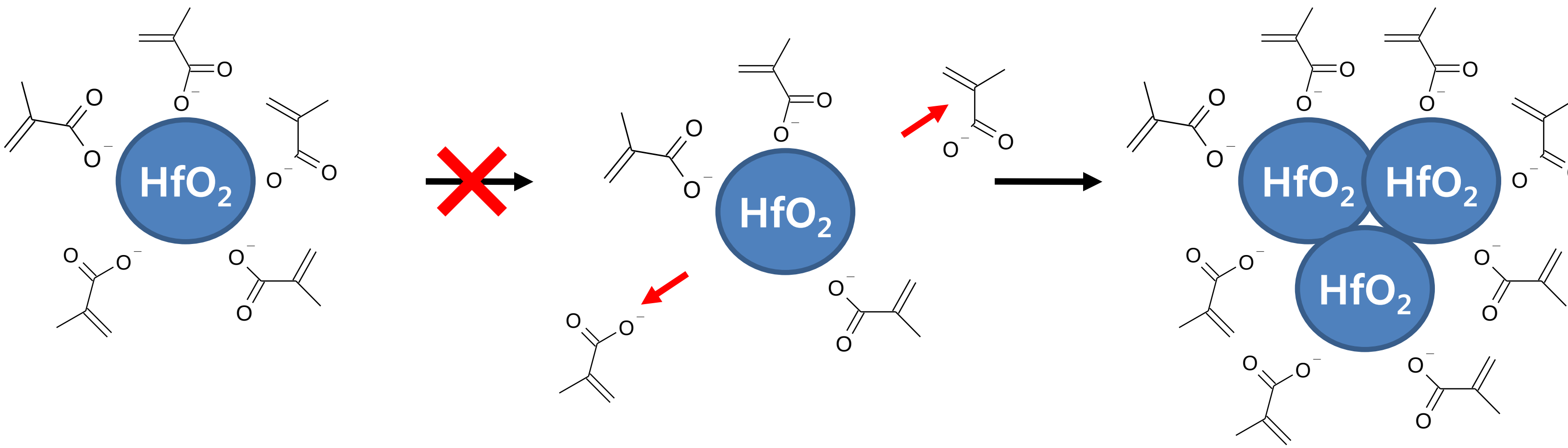
> +5.9



> +2.5

* Assuming an NMR minimum detection limit of 1%.

Ligand Binding Strength

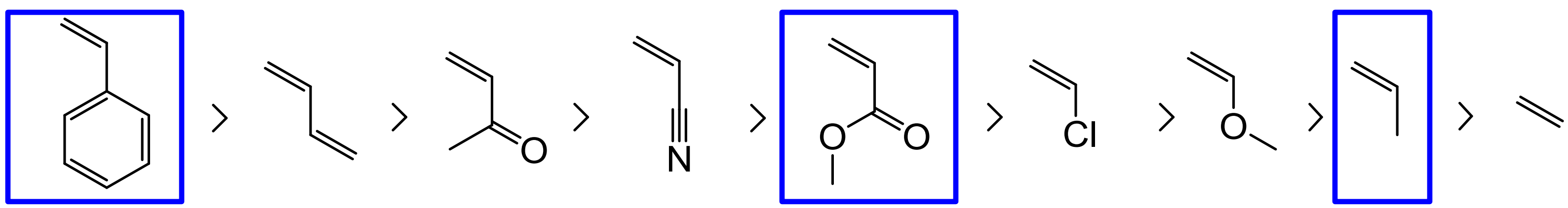


Without a strong ligand-nanoparticle bond, agglomeration can occur.

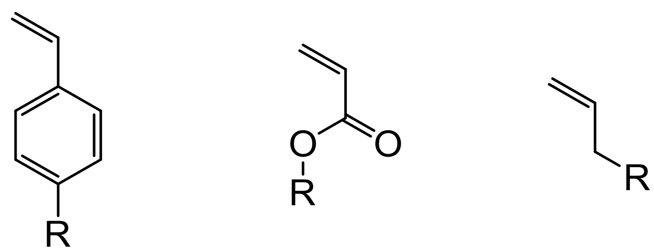
Plans to increase bond strength include:

1. **Ligand binding study (Thermodynamics)**
2. **Strong-binding free-radical monomers**

IV. Plans for Free Radical Monomer Ligands



Increasing Reactivity of Vinyl Monomers Under Free Radical Conditions



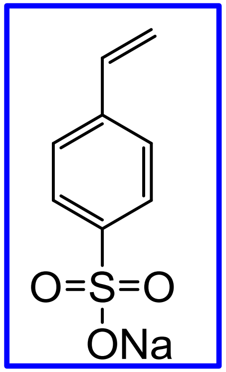
Three monomer types chosen for strong ligand binding study.

R = Strong Binding Group (i.e. –SO_3H, -PO_3H_2, etc.)

Mayo, Lewis, Walling ***"J. Am. Chem. Soc."****, 1948, pgs 1529-1533*

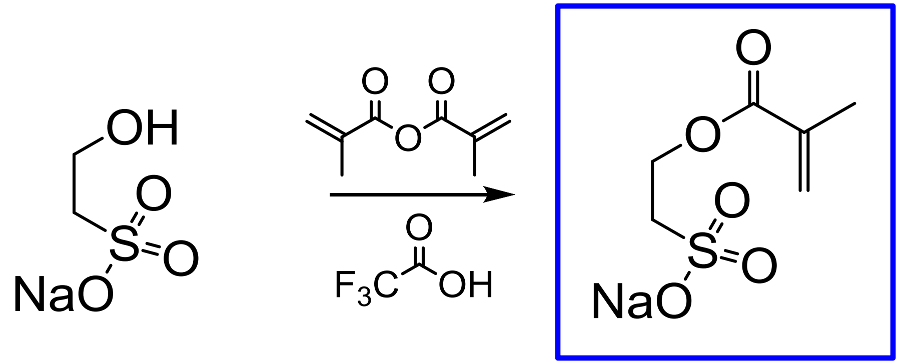
Strong-Binding Free-Radical Monomers

Sulfonates:

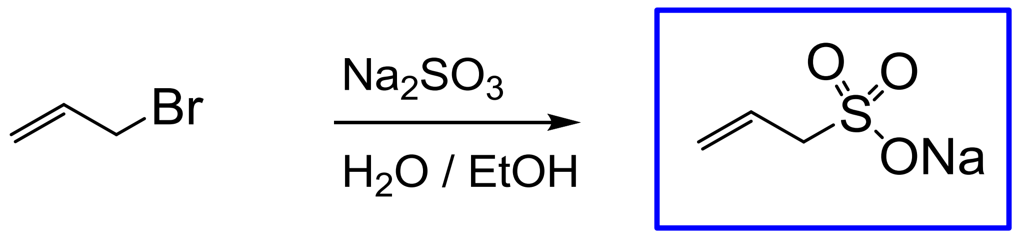


Commercially Available

Purchased

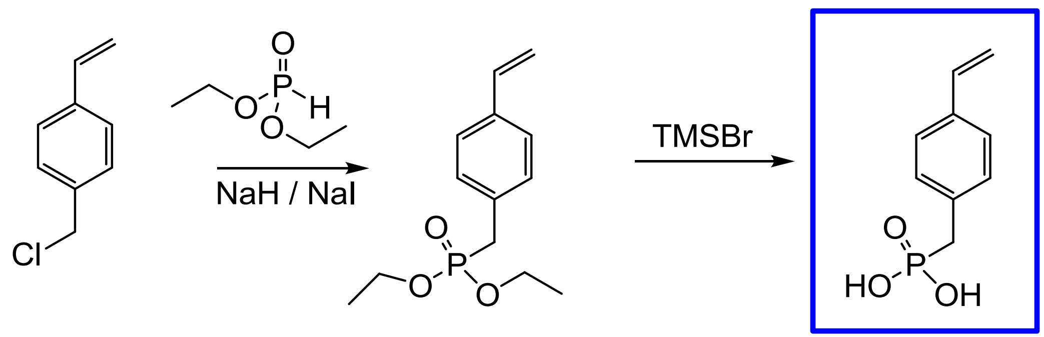


Made



Made

Phosphonates:

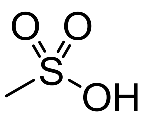


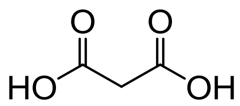
Although we were unable to quantify the relative binding energies of phosphonates, they seem to bind strongly, so we will prepare this ligand.

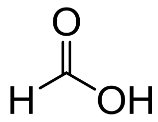
V. Summary and Future Directions

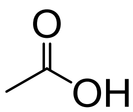
- We measured the equilibrium ligand concentrations for a series of ligands binding to hafnium oxide nanoparticles.

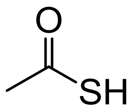
- For each of the ligands, binding energies were determined and compared.









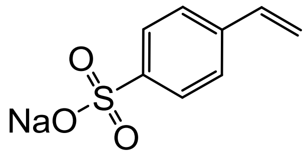


-1.96 **-0.41** **-0.30** **0.00** **+0.63[¥]**

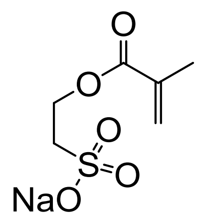
- Sulfonates were found to have the strongest binding energies with a relative energy of -1.96 Kcal/mol.

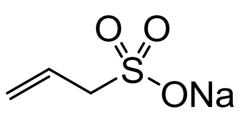
- We have designed a series of strong-binding ligands capable of free-radical polymerization.

- We purchased one of these ligands and made the other two and we are preparing to combine with the nanoparticles and evaluate as resists.



Commercially Available





Acknowledgements

Group Members Past and Present:

Craig Higgins

Seth Kruger

Srividya Revuru

William Earley

Avyaya Jayanthinarasimhan

Project Funding By:

SEMATECH

Accelerating the next technology revolution.

Staff at BMET:

Patrick Naulleau

Chris Anderson

Gideon Jones

Paul Denham

Nathan Smith

Lori Mae Baclea

And you for your time…

Appendix

Challenges to Precipitation

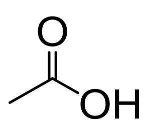
1. Nanoparticles of both ligands must precipitate in the same solvent.

	Water	Methanol	CH_2Cl_2	Hexane
Acetic Acid	X	X	X	
Formic Acid	X	X		
Chloroacetic Acid		X	X	X
Trifluoroacetic Acid		X	X	X
Malonic Acid	X	X		
Thioacetic Acid	X	X	X	
Methane Sulfonic Acid	X	X		

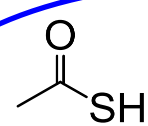
"X" indicates Solubility

2. Nanoparticles must precipitate independent of free ligands.

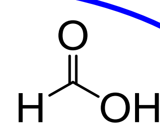
3. The two ligands must be separable by NMR.



2.0 ppm



2.2 ppm



9.0 ppm